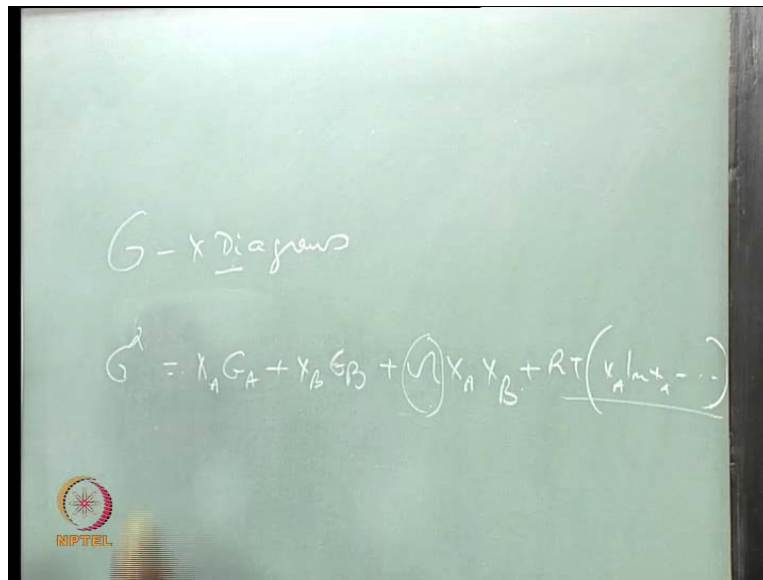


Advanced Metallurgical Thermodynamics
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Lecture No. #07
Evolution of Phase Diagrams

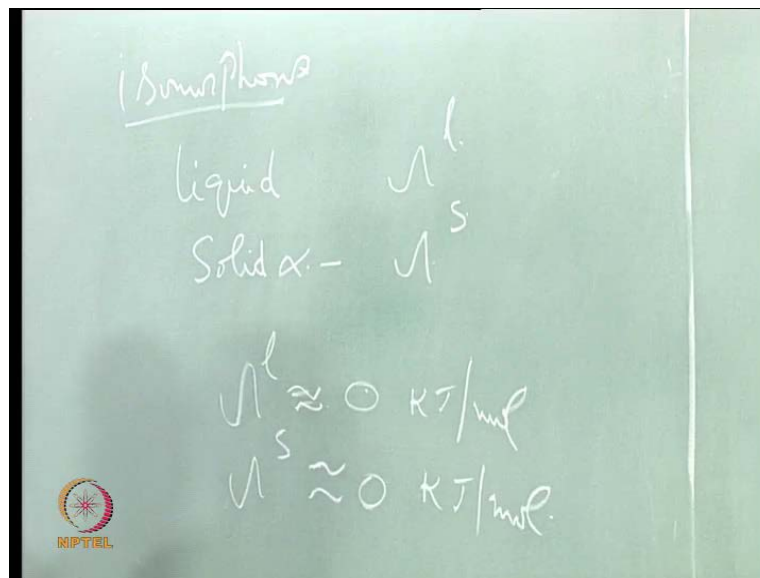
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Last class, we were talking about free energy composition diagrams; we also looked at how to get free energy composition diagrams, calculate them, also correlate them to phase diagrams **which to**, for example, an example of an isomorphous diagram. And then, we looked at how at various temperatures G-X diagrams can be obtained by calculation of the free energy as the function of composition at a given temperature, and from that, we can obtain what is called the solidus and the liquidus compositions at each temperature, because at each temperature you can get what is called the equilibrium between the two phases - the liquid and the alpha - and from that, in principle, we can generate the whole liquidus curve and the solidus curve, basically taking all these liquidus compositions at various temperatures, getting the trace of all these liquidus compositions at various temperatures; similarly the solidus composition at various temperatures.

Today, let us try to see, what is the correlation between these G-X diagrams; particularly looking at one particular parameters which is, **the, let us say** in any G-X diagram. For example, if you draw the free energy equation, if you remember, we talked about $X_A G_A$ plus $X_B G_B$ plus $\omega X_A X_B$ for a regular solution model of course; plus $R T X_A \ln X_A$ and so on, $X_B \ln X_B$. This is what we thought is then expression for the free energy of any phase and in this, what is known is this is absolutely no problem, at any given temperature, I can easily compute the last part; similarly, these two are the first two or basically the pure metal components, so it is this which decides to a large extent. What is the type of phase diagrams? For example, when you say an isomorphous diagram or a eutectic phase diagram or a peritectic phase diagram or even a monotectic phase diagram, they are all to a large extent decided by this. And let us see today, how this influences the evaluation of phase diagrams and see, how we can see various phase diagrams, with that particular ω as one of the component, for example, if you take an isomorphous system.

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All of you know there are certain conditions for you get an isomorphous system, what are the conditions? It should have same crystal structure and anything more, atomic radius different should be smaller and electro negativity and anything else, other than electro negativity atomic size structure valance **valance**. So, these are what we call them as **(())** rules, which decides that you get an isomorphous system and if you look at from the thermodynamic point of view, isomorphous system you have, whenever we are talking about isomorphous, we have

two phases: a liquid and a solid. So whenever I say a liquid and a solid, you can call it as an alpha phase let us say, for both of these phases I can write an expression like this.

Accepting that here instead of G_{α} I will put G_{liquid} and this will be $X_A G_A$ liquid, $X_B G_B$ liquid and this will be omega liquid of X_A and X_B and **and** so on. So, when you write two expressions for liquid and solid, you come across two omegas: one for the solid, one for the liquid, and they are not always the same. For example, if you take an example of a eutectic system, you know eutectic system, how do you define a eutectic? Anything beyond that is an invariant reaction let me see. What are all the possible ways of expressing eutectic, one is as you said, liquid giving to solids and it is an invariant reaction anything more. What is the eutectic? Melting point decreases anything beyond, when I say system A B system forms a eutectic, what do I mean? No, **no** let us not bring the thermodynamics at the moment, whatever let **whatever** they are immiscible.

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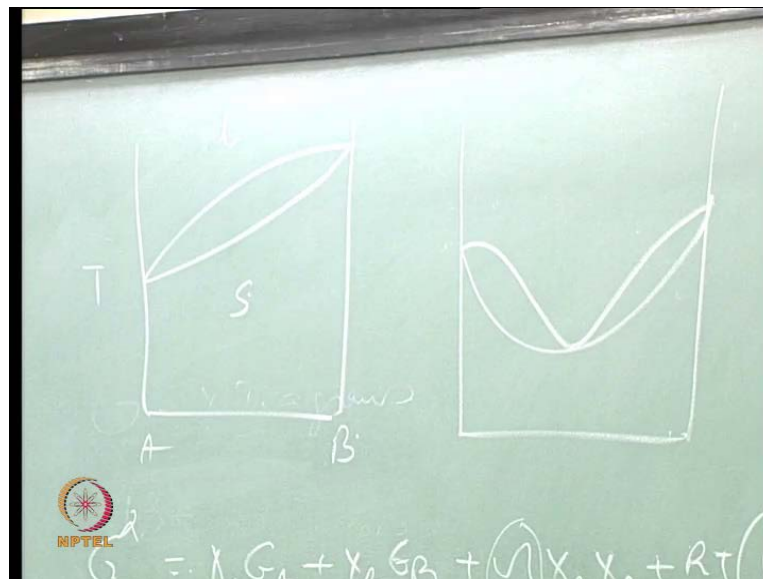
Makes the in what state, and the what about liquid? Yes, need not be completely insoluble, so the definition of a eutectic is A and B are completely miscible in the liquid state, they are either partially or completely insoluble in the solid state. I hope some stage you have read this, so if you have forgot it please brush it up. This is the definition of the eutectic, yes am I right? So, in the liquid state they are completely soluble, whereas in the solid state they are either partially or completely immiscible, so what that it means; that means, the omega are for that particular A B system.

In the liquid should be different from the omega in the solid, is it not? In case of a eutectic they are completely miscible or they are partially miscible and that means, there is a soluble limit be dissolves into A only up to certain extend, A dissolves into B only certain extend, that means there is a positive omega there, whereas in the liquid we are saying it is completely miscible; that means, possibly the omega in the liquid state is the either 0 or possibly close to negative or close to positive, but it is close to 0 because they are completely miscible, whenever we say completely miscible, it means the omega is close to 0, **whenever we say they are completely miscible**. That means, they are neither repelling each other nor forming inter metallic compounds. Whenever they form inter metallic compounds, ΔH is highly negative, that means omega is highly negative. So, whenever we see an isomorphous system, an isomorphous system basically indicates you this, **it indicates you this**, that the

omega of liquid is close to 0 and a omega solid is also close to 0, that is when you get a perfect isomorphous system which is this, where you have a temperature A B and this is a liquid and this is a solid.

The moment you see the phase diagram like that, you should understand that this is satisfied. The moment you see that one of this is 0, the other one is negative, for example, let us take a case of omega s being 0 and omega l is negative. What does that mean? It means the liquid is more stable with respect to the solid, liquid is more stable because liquid the free energy, it gives becomes more negative; that means, liquid is more stable with respect to the solid, that basically makes the liquid as plunge down.

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What you see the sudo eutectic kind of phase diagrams that, were you see this kind of a phase diagram is a result of this. It remains still isomorphous, but the liquid stability region is larger now, so the liquid exist over a range of higher range of temperature, when compared to what you see in a normal case like this. So, the liquid as goes down and that gives you an indication that liquid is more stable with respect to the solid.

And if you take another case, were omega l is 0 and omega s is negative. Then you get a congruent melting, this is what you see, you get a situation something like this. The solid is more stable with respect to the liquid, so solid tries to be an existing up to higher and higher temperatures and you immediately see a phase diagram like this. So, the moment you see the phase diagram, it gives you an idea even without doing calculations, it gives you an idea of

what you have been the thermodynamic parameters for the both the liquid and solid; now we have looked at only the negative aspect of it.

Now if you think of a situation where, **if you think of a situation where** the ω_l is 0, but the ω_s is positive, that actually means that both the A and B there is no attraction between them, there is some repulsion between them. And this basically means there is a tendency for segregation A does not want to dissolve B to a large extent and B does not want to dissolve A. And this actually needs you to what is called a miscibility gap in the phase diagram, for example, if I draw a isomorphous you suddenly start seeing a miscibility gap. If **you if** I try to correlate this with respect to what we talk about, **(())** parameters let us take one parameter such as a size factor.

You know that isomorphous actually happens when of course, this is more of a empirical rules, but in a large number of systems this is valid, when the size factor which is called the delta, δ is nothing but, the **the** atomic radius of the solvent minus the atomic radius of the solute divided by the atomic radius of the solvent, the absolute value of it, if this is less than 8 percent that is when you have a complete solubility.

When you have, let us say particular A B let us take a case of simple case of let us say, copper gold they are completely isomorphous, instead of copper gold, I add copper aluminum let us say both are fcc, but you do not see a isomorphous between a copper and aluminum, the reason could be because of many factors; and if we think that it is the size factor which is the size factor which is affecting it, let us assume a case of A B system with the size factor around 10 percent let us say. Then what you suddenly see is that, because the size factor is larger, the A dissolves, whenever a solute goes into the solvent as long as the solute size is closer to that of the solvent size, the strain that is generated is very **very** small. Whenever you imagine a case, where you have a lattice structure like this, imagine that these are all the atoms of the solvent and suddenly I want to put a solute inside this.

Assume that these are all of the same size, though some of these do not look like that or ignore that and now you think of a solute been put here. If this solute is of a smaller size than that of the solvent then what you see is, it tries to in order to maintain the bond, it tries to pull the atoms which are around it and that creates certain strain. Every 1 percent of the solute that we keep on putting you will keep seeing that, there is certain amount of strain that is generated and as you keep on increasing the amount of solute, the strain that generated gets

keeps on increasing; and any structure can accommodate up to certain amount of strain and the more close tag the structure is the less is the amount of strain that you can accommodate.

That is why bcc structure can easily accommodate more strain whereas, the fcc structures do not of course, again it depends on whether we are talking of what is called substitution solid solution or interstitial solid solution. Many of you remember that, carbon goes more into an fcc structure than into bcc structure; though fcc is more closed packed and the bcc you see the amount what is the solubility of carbon in fcc iron, 2 percent. What is it in a point? This 0.25 is the maximum in a bcc, so you see almost 80 times higher. This large quantity is basically because you see the voids, because it is a interstitial solid solution the void size in an fcc which is octahedral voids are much bigger than the biggest void, that is available in the bcc which is the tetrahedral void; and as the result because the voids being bigger the **the** carbon can go and sit.

And in fact, if you look at the actual carbon atomic size, the size of the carbon atom is much bigger than the void size and that is the reason why you do not see 100 percent solubility of carbon, in even fcc iron only 2 percent, and that if you compare with many substitution solid solutions, where you have isomorphous phase diagrams, **you have** you do not have an isomorphous phase diagram with an interstitial solid solution. It is impossible, because the only four elements that we talk about which can actually go into the interstitial solid solutions which are these elements, yes.

These elements that we talk about none of them have their sizes, which are so small that they can actually completely dissolve by 100 percent. This is streamer generated is sufficient enough that even if you put large quantity of this, the strain can be accommodated. So, if you look at the strain that it is, if you can think that there is a critical strain ϵ_{star} which a structure can accommodate; and if you think that there is particular strain called ϵ_1 , which is the amount of strain that is generated for every 1 percent of solute being going into the solvent, you can say this, this multiplied by this cannot cross this, this is the maximum that the solute can take. So if this is larger; that means the strain generated for every 1 percent of the solute is larger than this has to be smaller for a given structure.

For example, if I take a copper as a **as a** solvent and keep on adding element such as aluminum, lead and all other fcc elements, depending on the size factor between the copper and any of these solute atoms, you see the one which has a higher size factor, the solubility

limit of that particular solute will be smaller. Because this if this is larger than the maximum solute it can go is smaller, so that this is cannot be crossed, this is the maximum because the moment you cross this, then what the solvent does is it cannot take the solute anymore, so it starts rejecting it out and once it is rejected, you get various precipitates for example, in copper aluminum you get CuAl₂ and things like that. So, in different **different** phase diagrams we have different **different** phases coming out.

So, that limits what is called the solubility limit, so there is a critical strain any structure can accommodate and in fact, this what is also a reason, when you keep on putting more and more defects into a system, a crystal structure can even break and become amorphous. A large number of people studied this what are the conditions under which a crystal can be **(())** for example, the experiments were people have done taking a crystal and putting it into an electron microscope and keep on bombarding it with electrons, high energy electron beam particularly people have done this experiments with a high voltage microscopes.

I do not know whether you are aware there are microscopes which are 1000000 volt microscopes, 3000000 volt microscopes, 3000 kv in comparison to what we regularly see 100 kv or 200 kv or 300 kv microscope. We are talking of 3000 kv microscope, and when you have such a microscope where the electron beam of that energy solves onto a sample obviously, it disturbs the atoms. And as a result, you can have a large number of vacancies that are generated inside and if this concentration of vacancies keeps on increasing beyond a limit, the structure becomes unstable and it becomes amorphous.

So, people have seen cases where even an ordered structure, people are very interesting example people have taken is Ni₃Al which is an ordered structure, do you know what kind of an order structure it is, anybody knows? It is an fcc structure which is ordered and when it becomes ordered what do you call that structure, it **it** is called **called** L1₂ structure some of you know about structures is called L1₂ structure and this L1₂ structure were you have the nickel atoms occupying the **the** phase center positions and the aluminum atoms occupying the body corners; because it is Ni₃Al, 3 atom of nickel and 1 atom of aluminum.

This structure when they have taken and put it into such a high voltage microscope and with more and more dosage are this electron beam, they saw the slowly this ordered structure becomes disordered structure; that means, the superlattice changes into a disorder structure. That is whatever superlattice reflections that usually see in an ordered structure the slowly

start vanishing. If you initiate you can see this in a T E M. So, keep on observing how the diffraction pattern changes you see the superlattice reflection slowly vanish and only the fundamental reflections you see; that means, the ordered structure has become a disordered crystal structure, but still it is **it is** structurally ordered whenever you talk of disordering many of you might know that there are two types of disordering we are talk about - structural disorder, chemical disorder.

So, whenever I talk about ordered compound I am talking about chemical order there. When I say structural disorder it basically means a crystal structure a becoming into an amorphous structure that is a structural disorder. When I say chemical disorder that basically means in a in a chemically ordered compound, you have specific positions for each of the atom, let us say in this Ni_3Al just now I told you, that nickel occupies the phase centered positions, the aluminum occupies the body corners. If the aluminum and nickel randomly occupy the atomic positions inside the crystal structure, **the crystal structure** still will be fcc, but which will not called an ordered crystal anymore, it will be a disordered compound, because nickel and aluminum the probability of finding it in any place will be equaling to 2.25, 1.75 depending up on the amount of it, but I cannot pin pointedly say that this is where nickel is sitting, this is where aluminum is sitting, but in a ordered structure I can think pointedly say, this is where aluminum is there, this were nickel is there.

And so such a structure is a disordered structure chemically, but structurally sit it is ordered in the sense it has a unit cell it has a fcc unit cell, so this the difference between this chemically ordered and chemically disordered is only in terms of the refraction patterns, you can recognize you will see a extra parts called superlattice reflections in a chemically ordered structure and in a chemically disordered structure you will not see these extra parts; and you do not be see any of you who have read extra diffraction will know more about it, and now if you take that and if you continue to bombard it people have seen that disordered Ni_3Al , finally becomes an amorphous structure with 75 percent of nickel atoms and 25 percent of aluminum atoms, which are randomly their sitting inside without any unit cell, so the unit cell breaks a from a fcc unit cell to a structure which similar to that of liquid, and people have seen this happening and that is all because there is a critical strain that the structure can take, so if you look at from physical point of view it is like this.

But if you look at from the thermodynamics point of view we are looking at only from this and you know that the more the **the** strain is, when will the strain will be more, when the size

factor is more, so the larger the size factor you will see the larger will be the omega s positive, **sorry** I am extremely sorry for this.

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So, you can see that the moment size factor increases if the delta increases then you see omega s increases, higher and higher repulsion between the A and B as because as the size factor increases then the strain increases, if the strain increases; obviously, the repulsion increases, so now, we do not look at this part we simply look at what happens to the omega s increases, so the moment omega s is positive what you see is suddenly you see miscibility gap, as long as the size factor is less than 8 percent you will never see this miscibility gap, the moment size factor crosses 8 percent, you start seeing a miscibility gap; that means, what that means, there is a limit on the amount of B that can go into A.

So, only up to this much the B can dissolve into A and only this much is A can dissolve into B and whenever you see a solubility limit of A in B and B in A, you would see that this solubility limit keeps on changing as you change the temperature, why? so yes this epsilon star would change other function of temperature, the strain that the structure can accommodate because a lattice expands as the temperature increases, is it not? Because the lattice has expanded, so it can actually accommodate more and more strain and as a result, you would see as you increase the temperature the solubility limit keeps on increasing; that means, the amount of B that can dissolve into A keeps on increasing upto a particular limit, beyond which they are completely soluble, A becomes completely soluble in B and B becomes completely soluble in A. Similarly, on the other side also the solubility limit of A in B also keeps on increasing and you would see that, it will finally meet, and this is what is the final temperature, above which, you can say completely they are miscible and for a given omega this temperature is going to be fixed.

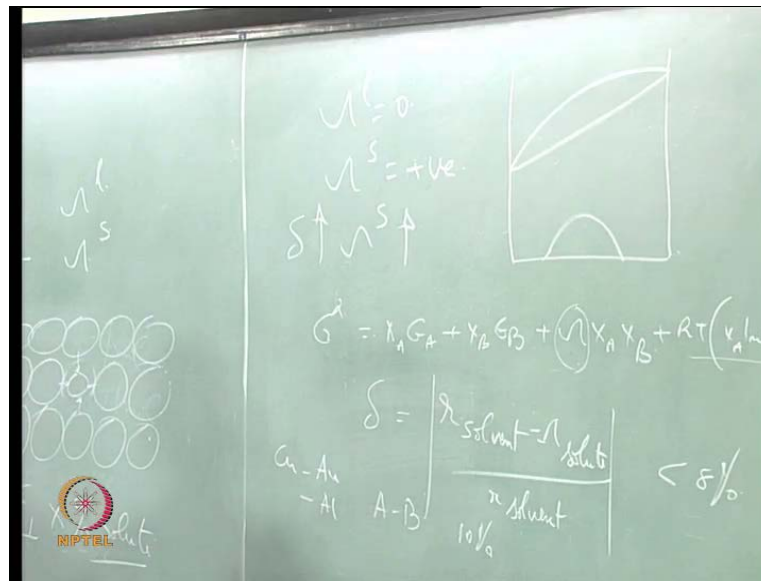
Now, for example, if you think of a particular value of omega let us say talk about 10 kilo joules and now you increase into 20 kilo joules or more, both being positive what should happen now, when you increase the omega s from 10 kilo joules to 20 kilo joules what should happen, yes the miscibility gap should widen, why because the **the** A and B are more and more repulsive, they are no more attract, so as a result the solubility of A in B and B in A should further go down, because A and B are **are** they repel each other to a larger extend and as a result, what you see is that this miscibility gap increases and the moment miscibility gap

increases, I mean in other words that when I say that means, size factor has further gone up, when the size factor further goes up this is what happens, is the size factor goes up here what happens is this will go up.

If this will go up for the same structure because we are assuming that our solute is the solvent is the same, if the solvent is the same solvent has the fixed a structure, so the total strain that it can accommodate is going to be fixed, so the epsilon star gets fixed the moment I fix up my solvent, what I am changing is only the solute, I am adding different **different** solutes each of them have a different size factor that means, each of them have a different omega positive, I am adding a different solute every time with a higher size factor such that it is omega s is more positive and that means, the moment this is higher because this is fixed this has to be lower.

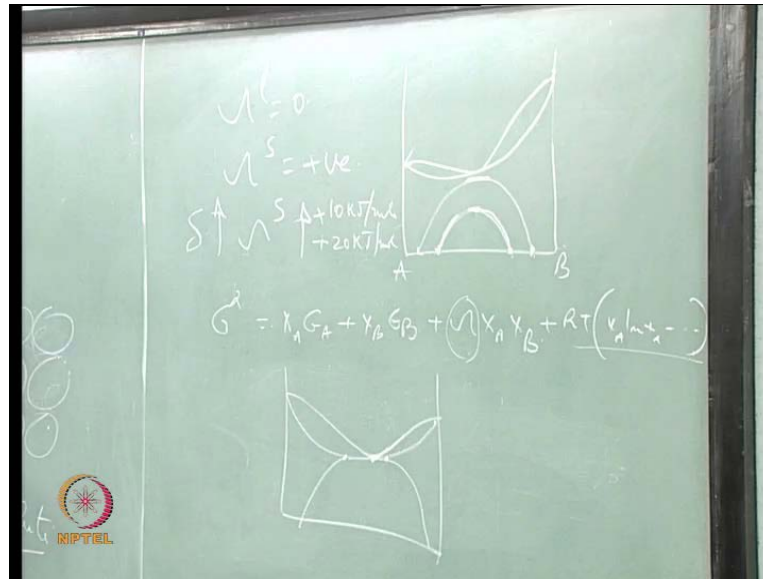
That's what, so we will come to it that means, what you would see is the, because this is fixed and at the same time you would see that the solubility limit and both the sides has come down that means, the strain that **that** each percentage of A, when it is added to B or each percentage of B when it is added to A is increasing, this value is increasing as a result for the same amount of this structure, when you are increasing the temperature this strain that it can accommodate is fixed this is fixed, but as you increasing the temperature because this strain is larger, the temperature to which you have to heat, so that the strain gets accommodated has to increase, as you keep on adding an element with higher and higher size factor, the temperature above which they completely dissolve into each other, should keep on increasing and that is why you would see that not only the solubility of A in B and B in A decreases, but also you see, the miscibility gap will go to higher and higher temperature and you would see that, the moment you start seeing bigger **bigger** miscibility gaps, its basically indicates that this is **(())**, but simultaneously.

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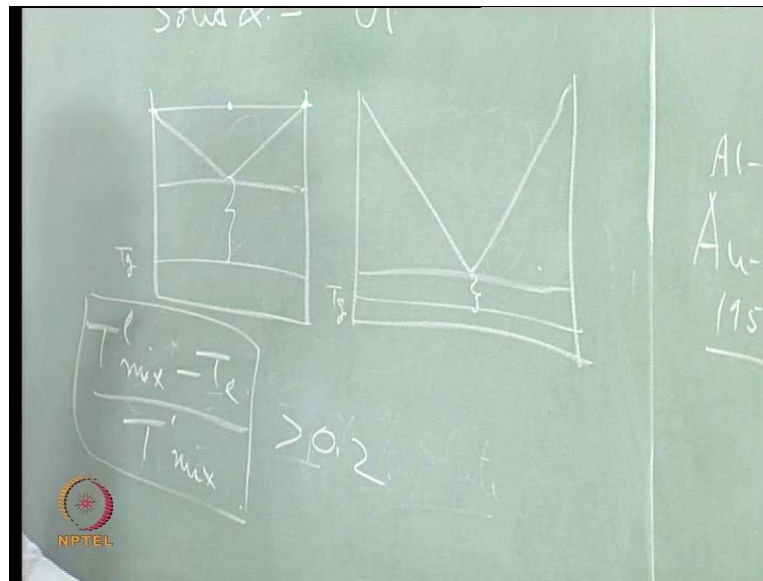
You would see something else also happens in the phase diagram, whenever you consider omega liquid being 0 and omega s being positive, you would see that not only that you develop a miscibility gap, but something happens to the liquid as curve also, what you would see is because the omega is positive and omega l is 0, so with respect to the solid the liquid is more stable and as a result what you would see is that, in addition to this you would see that this liquid as curve starts plunging down, because with respect to the solid, now the liquid is more stable, liquid is more negative with respect to this, if this is positive and this is 0 that means, it is more stable, so as a result liquid comes down, liquid is stable, over a larger temperature range and once this happens, you would see that there is a particular condition at which both these visibility gap and the liquid as merge into each other, and once that happens you would see a situation, where the phase diagram actually becomes and you would see both of them merging into each other and once they merge into each other what you end up is nothing but, eutectic you would see this is.

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This is nothing but, the eutectic point, these two are the compositions where you have actually the on the maximum solubility of B in A and maximum solubility of A in B, so you can see an isomorphous system suddenly has become a eutectic system, just because I have increased a ω_2 to a critical value and this at what a ω_2 this happens actually depends on system to system, each system you have to calculate and, but at a particular ω_2 you would definitely see this happening for everything and now, if you keep on increasing it further, more and more ω_2 what should happen to this, you would see two things happening, let me see what are your answers yes, so what does it mean, it means that the eutectic temperature goes down, this is what we call them as deep eutectics, whenever you see a deep eutectic, what we mean by deep eutectic, in fact people even quantify this eutectic, because it is very important when people talk about glass formation I will tell you an example for example.

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If you take two cases, **take a two cases**, one where the eutectic is like this, another where the eutectic is like this, we call this as a deep eutectic compared to this and in fact, people try to quantify this in terms of what is for taking the two pure metal melting points, calculating drawing that by a straight line and finding out, what is the liquid as temperature as a rule of mixtures of these two that means, at the eutectic composition.

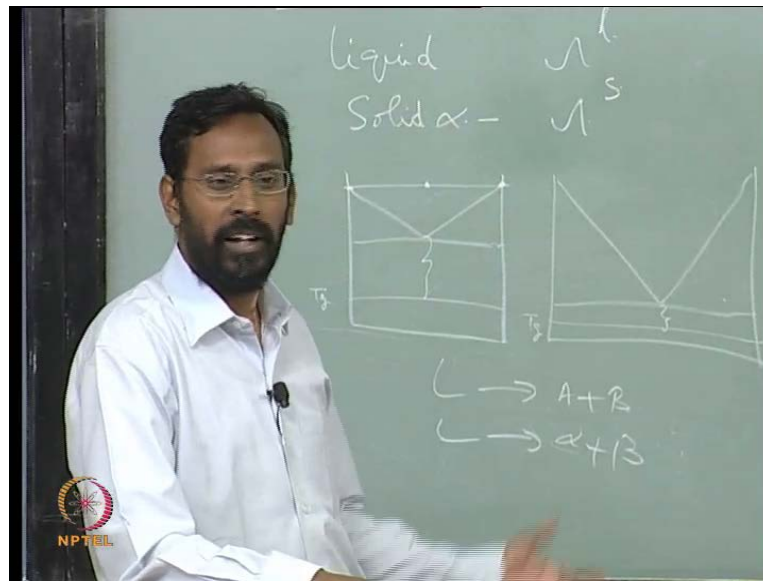
What should be the liquid as temperature, if liquid A and liquid B mixture is available let us say and that with respect to this, so we call it as $T_{mix} - T_{eutectic}$ divided by T_{mix} , as a parameter which people define it as a glass formation parameter, why it is important is when does a glass form, you said glass forms whenever a liquid is under cool to an extent, that it is brought below the T_g , in any system the T_g is somewhere here, glass transition temperature can always be calculated for a given system and usually a glass transition temperature is somewhere around 200,300 degrees depending on the particular system of course, there are some systems it can be even lower, when the liquid is very highly stable and then you would not see the glass formation easier, so if you think of a glass transition temperature somewhere if you have a phase diagram like this, it means the liquid for it to be under cool to get a temperature to T_g , **the** the temperature that you need to under cool is much smaller than here where the under cooling that we need to provide is very large; that means, the cooling rate that you need to provide for the liquid to under cool to the T_g is much larger here, when compared to the cooling rate that we need to provide for the liquid to under cool to T_g , that is why in a deep eutectic systems, we can always say glass formation

is easier, so that is why these are called easy glass forming systems, these are not so easy glass forming systems.

So, even with slower cooling rates people are able to achieve glasses for example, something like a silicate glass that you see a silicate glass can easily form a glass, even at a very very low cooling rate as low as even 0.1 kelvin per second whereas, a normal metallic glasses you need to go to 10^6 kelvin per second, to in order to be able to get that, that is the reason is because most of them, but even there also if you look at phase diagrams look at a number of phase diagrams, wherever you see a deep eutectic for example, the first metallic glass, when you when knows which is the system where people have got a first metallic glass, gold silicon, correct gold silicon is the first metallic glass in 1959, all do way has obtained it and this gold silicon if you compare it with simply like something like an aluminum silicon, today evening if possible go to the phase diagrams handbook such as (()) and try to compare gold silicon with aluminum silicon, you would see this is the much deeper eutectic than this, and that is the reason why you get a glass more easily here, than that you take a simple aluminum silicon liquid and of the eutectic composition simply quench it, you would not be able to get a glass there whereas, here if you quench that liquid, you can get a glass, so that is basically because this is deeper eutec and people have given a condition that, if this value is greater than 0.2 by looking at a number of systems, people have said that if this value is greater than 0.2, than you can say it is a easy glass forming system, otherwise it is not so easy glass forming system of course, these are some rules like a (()) rules more of the empirical rules, based on looking at a number of systems and people have come across certain values like that.

So, this is one of the glass forming criteria, there are number of them we will talk about them as we go along a little later, so just because this concept came I have to tell you this, so as you can see, that if I keep on increasing omega you would see just goes down and as the result you would see that the liquid as temperature goes to lower and lower value that means, eutectic temperature goes to lower and lower value and anything else that happens, so that means the solubility limit of A in B and B in A also starts decreasing further, because this increases means this becomes more, so that kind of thing you would see, so the the because the miscibility gap becomes wider and wider.

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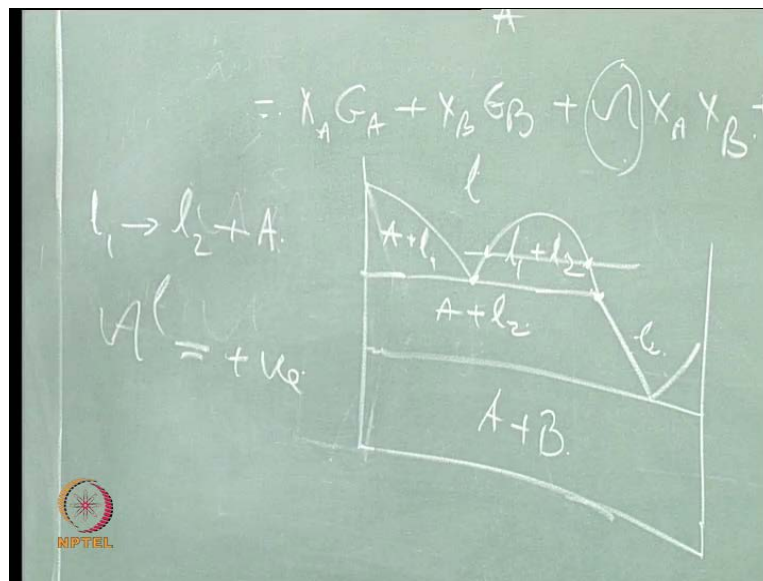
So, solubility limits keep on decreasing to an extent that had some value, you would see that the solubility limits vanish something like this, you see a phase diagram become something like this, where there **there** is no solubility of B in A or A in B, it is like a liquid giving A plus B instead of liquid giving alpha plus beta, so the difference between the two is it not? When I say liquid giving alpha plus beta that means, the two are terminal solid solution that means, there is a solubility of A in B and B in A, so instead of a phase diagram like this, you end up into a phase diagram like this.

Something like this, a there is no solubility of A in B, so the moment you see these things, you can get an idea of these and people actually even do the calculations to be able to find out whether it really happens or not, and **and** a number of people have already done this and as I told you, even we have a journal which is available for cal fact which regularly does this kind of calculation and now let us see what happens, if the omega I is positive, yes pure iron, it is because of the magnetic transitions, you know in principle that iron is bcc at room temperature know and then it changes to fcc and then. In fact, if you carefully observe most of the actual metals, when you go to a higher temperature the **the** phase that is more stable is a one which have more open structure, you regularly see this happening in **in**. For example, titanium high temperature phase is a bcc phase, in most of the structure the high temperature phase is always a bcc phase even if you look at things like ceramics **(())** we take high temperature phase is always a cubic phase, low temperature phase tetragonal phase, even if

you take the zirconia, titania and eutriya all these things you see this kind of things were as here.

Because there is a magnetic transition, that interferes with that, so as the result you get that and because that phase is actually not a close pack structure is not really stable at high temperature, so when you further heat it to high temperature it comes back to an open packed structure, which is the bcc structure, so the intermediate fcc structure is the result of actually magnetic transition in this material, otherwise you would not have seen this.

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So now, if you look at this case of, if I assume a case of like this which I cannot actually assume, this actually looks upset to anybody, but why should it look upset, when I say omega is equal to 0 omega is positive, you say that when you say omega is positive that means, A and B are **are** repelling each other in a liquid state, if A and B repel each other in a liquid state automatically they actually repel each other in the solid state also, is very **very** difficult to imagine that A and B are having an ideal kind of a situation, they neither repel nor attract in a solid state, but in the liquid state they repel each other, because a liquid is a more open structure. In a more open structure actually A and B should dissolve more easily, that is why we see whenever I say eutectic by the way when we talk about this, the eutectic formation from an isomorphous, you can also get a peritectic in the same fashion, they are expecting the difference is you get a peritectic, when the melting points of the A and B are largely different.

Same way you can construct and you can get a very peritectic diagram from an isomorphous phase diagram, excepting that the peritectic happens when the two (()). For example, whenever you see a peritectic a good example is copper zinc let us say, copper zinc is a classic example of what people are calling as cascade of peritectic, we have a number of peritectic in a copper zinc, copper tin is also another such example that is, the reason is one of the element copper melts at a much higher temperature than the tin which melts at a let us say 232 degree centigrade also, so when you see this large differences in the melting point, then instead of a eutectic you see a peritectic happening. And you would see if you go back to any of the phase diagrams, you will see this happening now coming back here, you see that if this has to happen hypothetically anything can be assumed, if you assume this hypothetically what it means is, if the omega 1 is positive that means, there is a miscibility gap in the liquid, have you heard of miscibility gaps in the liquid, where do you see miscibility gaps in the liquid, monotectic phase diagram is one of course, the extreme of this is a syntactic, so monotectic for example, if I draw a monotectic phase diagram, what is a monotectic phase diagram, this is the monotectic.(Refer Slide Time: 43:14)

That there is a liquid and here you have $l_1 + l_2$, so what does the this reaction means l_1 gives you, what is a monotectic reaction, how many of you remember, yes liquid gives another liquid plus a solid, this can be an alpha this can be a pure metal depending on the situation, most of the cases the solubility of B in the solid in many of the monotectic system is almost 0, so we can a simply say that these gives you a solid A let us say, A or B depending on which side the monotectic is so that means, this phase diagram can be replaced by something like this. That is low solubility on this side and as a result you can say liquid gives A plus liquid 2 and now whenever, you say liquid 1 gives you a solid plus another liquid that means, below the reaction and again this is also is an invariant reaction like what we have seen earlier, why it is an invariant reaction, why 0 degree of freedom, three phases we have and it is a binary system, **it is a binary system** number of components are two and we have three phases involve, why I say three phases because there are two liquids, what is the difference between the two liquids, concentration the composition of l_1 is different from composition of l_2 both having the same structure, **both have the same structure** they are all both of them are liquids, so they have random arrangements of atoms, but they have two different compositions.

And the moment I say two different compositions there is a boundary between them and as a result I have to define it as a separate phase, so that is why like **like** here when I say a miscibility gap in an solid state, what is there between in within the miscibility gap, two solids, we call them as alpha 1 plus alpha 2 and interestingly both of them have the same structure, because on the both the sides two pure metals have the same structure otherwise you would not have got a isomorphous system, the fact that it is a isomorphous it indicates that A and B are the same structure, we are only talking about A and B and the same structure, but with different atomic sizes such that you are getting a miscibility gap or with whatever may be the parameter, whether it is atomic sizes or a no valency or electro negativity, but ultimately giving to a positive omega s, we have only taken a size factor as one of the parameters is because it is easy to see, because it is easy to understand based on the strain whereas, the other two I can also choose electro negativity or valency, but again the same thing has to basically everything gets reflected to this, if this becomes positive you get though A and B have the same structure, you get a miscibility gap and in within that, both the alpha 1 and alpha 2, that you see are the same structures, but accepting that their compositions are different that is why, if I draw at any given temperature a tie line here these two points represent.

The composition of alpha 1 and composition of alpha 2 exactly similarly, if I draw at any given temperature here, these two represent this is the composition of l 1, this is the composition of l 2, and at the peritectic at the monotectic temperature l liquid of this particular composition is giving you another liquid of this composition And because below the monotectic there is a liquid that is available, because one liquid is giving you another liquid, this liquid which is coming out of the monotectic has somehow to solidify, so as a result many monotectic phase diagrams, you would see medicine to monotectic reaction another additional reaction were the liquid, which comes to of the monotectic solidifies by either a eutectic reaction or by a peritectic reaction. So, that is why you would see here, an extension of it, you would see an either a eutectic reaction so that means, here the l 2 that is coming out, here you can say it is A plus l 2 below the monotectic reaction. So, liquid gives you and this is what **what** is faze field, A plus l 1, so you will have A plus l 2 and this l 2 will undergo a eutectic reaction or a peritectic reaction in this particular case it is a eutectic reaction. And as a result below that eutectic reaction, what will you have A plus B simply, that is how we can see whereas, if it is a eutectic reaction or a peritectic reaction, you need not have to have another reaction, there can be phase diagrams were you can have a number

of various reactions like iron carbon where you have a eutectic peritectic and eutectoid, but there are also systems where you have only one simple reaction for example, aluminum silicon, it has one single eutectic nothing else, magnesium silicon we have two eutectics nothing else.

So, there are also systems like this, so you will see whenever you see a monotectic you will see things like this, and this monotectic is caused by what, the ω_1 being positive, whenever ω_1 is positive, there is a miscibility gap inside the liquid and once there is a miscibility gap inside the liquid, you need to monotectic reaction and that is how, we can understand and the more the ω_1 becoming more and more positive it finally, leads you to syntactic kind of case **case** where there are completely insoluble in the liquid state and also soluble in the solid state, you rarely can think of the situation, where they are completely insoluble in the liquid state, but soluble in the solid state, reverse is possible, that you can have a complete insolubility in the solid state, but solubility in the liquid state which is what is our eutectic, but you would not see the situation that why whenever there is a syntactic there is a complete insolubility in the liquid state, you also see that in the solid state, there is complete insolubility and that is how we can see just based on these two parameters we can evaluate these diagrams will stop now.